

09/744437

## TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 49288DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.  
PCT/EP 99/05933INTERNATIONAL FILING DATE  
13 August 1999PRIORITY DATE CLAIMED  
17 August 1998

TITLE OF INVENTION: PREPARATION OF ALKYNEDIOLS

APPLICANT(S) FOR DO/EO/US Alois KINDLER, Melanie BRUNNER, Christian TRAGUT, Jochem HENKELMANN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
  2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
  3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
  4. /x / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b./ / has been transmitted by the International Bureau.
    - c./ / is not required, as the application was filed in the United States Receiving Office (RO/USO).
  6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. /X/ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
    - a./X/ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b./ / have been transmitted by the International Bureau.
    - c./ / have not been made; however, the time limit for making such amendments has NOT expired.
    - d./ / have not been made and will not be made.
  8. /X/ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. / X/ An oath or declaration of the inventor(s) (35 U.S.C. 171(c)(4)).
  10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
11. / / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. /x / An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. / X/ A FIRST preliminary amendment.
  - / / A SECOND or SUBSEQUENT preliminary amendment.
  14. / / A substitute specification.
  15. / / A change of power of attorney and/or address letter.
  16. /x / Other items or information.  
International Search Report  
International Preliminary Examination Report

U.S. Appl. No. (If Known) INTERNATIONAL APPL. NO.  
PCT/EP99/05933ATTORNEY'S DOCKET NO.  
49288

17. /X/ The following fees are submitted  
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):  
Search Report has been prepared by the  
EPO or JPO.....\$860.00

CALCULATIONSPTO USE ONLY

International preliminary examination fee paid to USPTO  
(37 CFR 1.482).....\$750.00

No international preliminary examination fee paid to  
USPTO (37 CFR 1.482) but international search fee paid  
to USPTO (37 CFR 1.445(a)(2)).....\$700.00

Neither international preliminary examination fee  
(37 CFR 1.482) nor international search fee  
(37 CFR 1.445(a)(2)) paid to USPTO .....\$ 970.00

International preliminary examination fee paid to  
USPTO (37 CFR 1.482) and all claims satisfied pro  
-visions of PCT Article 33(2)-(4).....\$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860.00

Surcharge of \$130.00 for furnishing the oath or declaration  
later than / / 20 / / 30 months from the earliest  
claimed priority date (37 CFR 1.492(e)).

| Claims                                      | Number Filed | Number Extra | Rate            |
|---|--------------|--------------|-----------------|
| Total Claims                                | 8            | -20          | XS18.           |
| Indep. Claims                               | 1            | -3           | XS80.           |
| Multiple dependent claim(s) (if applicable) |              | +270.        |                 |
| <b>TOTAL OF ABOVE CALCULATION</b>           |              |              | <b>= 860.00</b> |

Reduction of 1/2 for filing by small entity, if applicable.  
Verified Small Entity statement must also be filed  
(Note 37 CFR 1.9, 1.27, 1.28).

**SUBTOTAL = 860.00**

Processing fee of \$130. for furnishing the English  
translation later than / / 20 / / 30 months from the  
earliest claimed priority date (37 CFR 1.492(f)).

**TOTAL NATIONAL FEE = 860.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)).  
The assignment must be accompanied by an appropriate cover  
sheet (37 CFR 3.28, 3.31) \$40.00 per property

**TOTAL FEES ENCLOSED = \$ 900.00**

Amount to be  
refunded: \$  
Charged \$

a./X/ A check in the amount of \$ 900. to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

KEIL & WEINKAUF  
1101 Connecticut Ave., N.W.  
Washington, D. C. 20036

*Herbert B. Keil*  
SIGNATURE

Herbert B. Keil

NAME

Registration No. 18,967

525 Rec'd PCT/PTO 24 JAN 2001

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of )  
 KINDLER et al. ) BOX PCT  
 )  
 International Application )  
 PCT/EP 99/05933 )  
 )  
 Filed: August 13, 1999 )  
 )  
 For: PREPARATION OF ALKYNEDIOLS )

PRELIMINARY AMENDMENT

Honorable Commissioner of  
 Patents and Trademarks  
 Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

1. In a process for preparing alkynediols by reacting ketones with acetylenic hydrocarbons selected from the group consisting of acetylene and alkynemonool in an organic solvent in the presence of a base comprising potassium alkoxides of primary and/or secondary alcohols to form adducts of alkynemonools and/or alkynediols and said base which precipitate from the reaction mixture, the improvement which comprises, using as acetylenic hydrocarbon acetylene in the ratio of ketone to acetylene from [1,9 to 2,1:1] 1.9 to 2.1:1 and the ratio of potassium alkoxide to ketone is within the range from [0,9 to 2,1:1] 0.9 to 2.1:1 and using as acetylenic hydrocarbon alkynemonool in the ratio of alkynemonool to ketone from [1: 0,8 to 1,2] 1.0.8 to 1.2 and the ratio of potassium alkoxide to ketone is within the range from [1,5 to 2,2:1] 1.5 to 2.2:1, so as to produce [gellike] gel like adducts having a spherical surface, whereby the reaction mixture remains stirrable during the entire reaction.
2. A process as claimed in claim 1, wherein, using as acetylenic hydrocarbon acetylene, it is used in a stoichiometric amount with regard to the ketone and ratio of potassium alkoxide to ketone is within the range from 1:1 to [1,5:1] 1.5:1.
4. A process as claimed in claim 1, wherein, using as acetylenic hydrocarbon alkynemonool the ratio of alkynemonool to ketone is within the range from 1:1 and the ratio of potassium alkoxide to ketone is within the range from [1,9:1 to 2,1:1] 1.9:1 to 2.1:1.
5. A process as claimed in claim 1 [any of claims 1 to 4], wherein ketones selected

from acetone, methyl isobutyl ketone and cyclohexanone are used.

7. A process as claimed in claim 1 [any of claims 1 to 6], wherein hydrocarbons are used as solvents.

8. A process as claimed in claim 1 [any of claims 1 to 7], wherein the potassium alkoxides used are potassium butoxides.


#### REMARKS

The claims were amended in the preliminary examination. The claims have been amended further to eliminate multiple dependency and to put them in better form for U.S. filing. No new matter is included. A clean copy of the claims is attached.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF

  
Herbert B. Keil  
Reg. No. 18,967

1101 Connecticut Ave., N.W.  
Washington, D.C. 20036

(202)659-0100

## CLEAN CLAIMS

1. In a process for preparing alkynediols by reacting ketones with acetylenic hydrocarbons selected from the group consisting of acetylene and alkynemonool in an organic solvent in the presence of a base comprising potassium alkoxides of primary and/or secondary alcohols to form adducts of alkynemonools and/or alkynediols and said base which precipitate from the reaction mixture, the improvement which comprises, using as acetylenic hydrocarbon acetylene in the ratio of ketone to acetylene from 1.9 to 2.1:1 and the ratio of potassium alkoxide to ketone is within the range from 0.9 to 2.1:1 and using as acetylenic hydrocarbon alkynemonool in the ratio of alkynemonool to ketone from 1: 0.8 to 1.2 and the ratio of potassium alkoxide to ketone is within the range from 1.5 to 2.2:1, so as to produce gel like adducts having a spherical surface, whereby the reaction mixture remains stirrable during the entire reaction.
2. A process as claimed in claim 1, wherein, using as acetylenic hydrocarbon acetylene, it is used in a stoichiometric amount with regard to the ketone and ratio of potassium alkoxide to ketone is within the range from 1:1 to 1.5:1.
3. A process as claimed in claim 2, wherein the ratio of potassium alkoxide to ketone is within the range from 1.1:1 to 1.3:1.
4. A process as claimed in claim 1, wherein, using as acetylenic hydrocarbon alkynemonool the ratio of alkynemonool to ketone is within the range from 1:1 and the ratio of potassium alkoxide to ketone is within the range from 1.9:1 to 2.1:1.
5. A process as claimed in claim 1, wherein ketones selected from acetone, methyl isobutyl ketone and cyclohexanone are used.
6. A process as claimed in claim 5, wherein acetone is used as ketone.
7. A process as claimed in claim 1, wherein hydrocarbons are used as solvents.

8. A process as claimed in claim 1, wherein the potassium alkoxides used are potassium butoxides.

As originally filed

---

### Preparation of alkynediols

---

5

This invention relates to a process for preparing alkynediols by reacting ketones with acetylenic hydrocarbons using potassium alkoxides.

A number of processes are known for preparing alkynediols.

15 Reppe's ethynylation process, reaction of aldehydes such as formaldehyde and acetaldehyde with acetylene over copper acetylide as catalyst, gives secondary alkynemonools and glycols in good yields. In the case of higher aldehydes, however, this method leads to  
20 unsatisfactory results.

The preparation of tertiary alkynediols by reacting ketones with acetylenic hydrocarbons using bases is particularly problematical. Most existing processes  
25 utilize finely divided, ideally water-free KOH powder in organic solvents such as THF, diisopropyl ether, dioxane, methylal or acetaldehyde dibutyl acetal. The disadvantage with these processes is that they mostly produce mixtures of monoalkynols and alkynediols  
30 containing an appreciable proportion of monoalkynols. A further disadvantage is that the suspensions formed in the solvents mentioned become so viscous through the formation of acicular crystalline adducts of KOH and tertiary monoalkynols and alkynediols that stirrability  
35 is appreciably compromised. As a result, efficient mixing and hence controlled dissipation of the heat of reaction is compromised or impossible. This leads to

safety problems as well as low conversions. A possible use of larger solvent quantities has relatively small effect on the viscosity profile and is generally uneconomical, since the solvents used are costly.

5

EP-A 0 285 755 describes a process for preparing tertiary alkynediols by reacting ketones with acetylene. In particular, acetylene is reacted with carbonyl compounds and KOH powder as base. Alkyl tert-butyl ethers are used as solvents. The ketone and acetylene are used in a molar ratio of 1 : 1 to 3 : 1 and KOH and ketone in a molar ratio of 1 : 1 to 1.6 : 1. The solvent used is set to ensure efficiently stirrable reaction mixtures. However, it proved impossible to reproduce the teaching of this application (Comparative Example 2). Another disadvantage with this process is the use of specific, costly solvents, making the process uneconomical.

20 DE-A 20 08 675 describes the preparation of tertiary alkynediols by reacting ketones with acetylene using potassium alkoxides of primary and secondary alcohols of limited solubility in water. Aliphatic, cycloaliphatic and aromatic hydrocarbons can be used as solvents. Similarly, DE-A 20 47 446 describes the use of potassium alkoxides for preparing alkynediols by reacting alkynemoneols with ketones.

30 In both processes, an increase in the viscosity of the reaction mixture in the course of the reaction is observed. Efficient mixing of the reaction batch and controlled dissipation of the heat of reaction are therefore compromised, so that the aforementioned problems arise in these processes, too.

35

It is an object of the present invention to provide a process for preparing alkynediols using an economically



acceptable amount of a common organic solvent. The reaction mixture shall remain efficiently stirrable during the entire reaction time, ensuring controlled dissipation of the heat of reaction and good conversions.

We have found that this object is achieved by a process for preparing alkynediols by reacting ketones with acetylenic hydrocarbons in an organic solvent in the presence of a base comprising potassium alkoxides of primary and/or secondary alcohols to form adducts of alkynemonools and/or alkynediols and said base which precipitate from the reaction mixture by selecting the stoichiometries for the reaction partners so as to produce gellike adducts having a spherical surface, whereby the reaction mixture remains stirrable during the entire reaction.

The adducts which precipitate are adducts of the base with alkynemonools or alkynediols formed in the course of the reaction. Provided a certain stoichiometry is adhered to for the reaction partners, these adducts are gellike and not acicularly crystalline. A spherical surface for the purposes of the invention is a rounded, preferably spherelike surface of the kind present in gellike adducts. This ensures that there is none of the intermeshing which appreciably compromises stirrability as in the case of crystalline, acicular adducts and that instead the precipitated adducts are able to glide past one another when stirred. This permits the controlled dissipation of the heat of reaction and distinctly better mixing of the reaction partners. As well as having an advantageous effect on the conversions of the reaction, controlled dissipation of the heat of reaction is also desirable for safety reasons. If controlled dissipation of the heat of reaction is not ensured, the decomposition temperature

of the substances present in the reaction mixture may be exceeded locally and this may give rise to spontaneous decompositions.

- 5 Acetylenic hydrocarbons for the purposes of the present invention are acetylene and monoalkynols prepared from carbonyl compounds and acetylene.

10 In a preferred embodiment of the process of the invention, acetylene is used as acetylenic hydrocarbon. Owing to the efficient mixing, the stoichiometry for the starting materials can be chosen in such a way that acetylene is used stoichiometrically with regard to the ketone. By stoichiometrically is meant a ratio of  
15 ketone to acetylene within the range from 1.9 : 1 to 2.1 : 1, preferably a ratio of 2 : 1. The ratio of potassium alkoxide to ketone is within the range from 0.9 : 1 to 2.1 : 1, preferably within the range from 1 : 1 to 1.5 : 1, particularly preferably within the  
20 range from 1.1 : 1 to 1.3 : 1. The alkoxide-to-ketone ratio chosen is an essential factor to ensure reaction mixture stirrability, since, at the ratio chosen, the adducts formed are not acicular but gellike and have a spherical surface.

- 25 The concentration of the reaction partners in the reaction mixture may be specified in terms of the weight ratio between ketone and a suspension of solvent and base. The concentration at which the reaction  
30 mixture remains efficiently stirrable depends on the reaction conditions and in particular on the ketone, solvent and alkoxide used. In the case of a suspension of potassium isobutoxide in xylene and acetone, the weight ratio between ketone and the suspension is  
35 generally not less than 1 : 2.5, preferably within the range from 1 : 2.5 to 1 : 8, particularly preferably 1 : 6.5.

In a further embodiment, the acetylenic hydrocarbons used are alkynemonools. Alkynemonools can be prepared by reacting acetylene with carbonyl compounds according to literature methods.

The carbonyl compounds used can be aliphatic and aromatic aldehydes and ketones. Preference is given to the use of ketones, with aliphatic ketones being particularly preferred. These can be linear, branched or cyclic. Preference is given to using ketones having from 3 to 8 carbon atoms, particularly preferably having from 3 to 6 carbon atoms, with acetone, methyl isobutyl ketone and cyclohexanone being very particularly preferred.

Accordingly, the acetylenemonools used are particularly preferably methylbutynol, 3,5-methylhex-1-yn-3-ol and 3-cyclohexylprop-1-yn-3-ol.

The ratio of alkynemonool to ketone is within the range from 1 : 0.8 to 1 : 1.2, preferably 1 : 1. The ratio of potassium alkoxide to ketone is within the range from 1.5 : 1 to 2.2 : 1, preferably within the range from 1.9 : 1 to 2.1 : 1, particularly preferably 2 : 1. The molar ratios chosen ensure reaction mixture stirrability and thus good conversions and controlled dissipation of heat.

The ketones used for the reaction with acetylenic hydrocarbons can be aliphatic and aromatic ketones. The use of aliphatic ketones is preferred. These can be linear, branched or cyclic. Particular preference is given to using aliphatic ketones having from 3 to 8 carbon atoms, very particularly preferably having from 3 to 6 carbon atoms. Among these, acetone, methyl

isobutyl ketone and cyclohexanone are preferred. The use of acetone is very particularly preferred.

- 5 Suitable solvents are in particular hydrocarbons and ethers. Preference is given to the use of aliphatic and/or aromatic hydrocarbons. Particular preference is given to hydrocarbons having a boiling range from 80 to 180°C. Very particular preference is given to aliphatic hydrocarbons such as gasoline mixtures, cycloaliphatic
- 10 hydrocarbons such as cyclohexane or aromatic hydrocarbons such as benzene, toluene, xylene, cumene or p-isopropylbenzene. The use of xylene is very particularly preferred.
- 15 The potassium alkoxides used are potassium alkoxides of secondary and/or primary alcohols. Alkoxides of C<sub>3</sub>-C<sub>8</sub> alcohols, which can be linear, branched or cyclic, are preferred.
- 20 For example, it is possible to use the alkoxides of primary alcohols such as n-butanol, isobutanol, n-pentanol, 2-ethyl-4-butanol, 2-methyl-1-butanol, 2,2-dimethyl-1-propanol, hexanol, 2-ethylhexanol and also the potassium alkoxides of secondary alcohols such as
- 25 2-butanol, 2-pentanol, 3-pentanol, 2-methyl-3-butanol and cyclohexanol. Particular preference is given to the use of potassium butoxides, especially potassium isobutoxide.
- 30 A process for obtaining the potassium alkoxides is described in DE-A 20 08 675. Aqueous potassium hydroxide solution (a 50% strength by weight aqueous KOH solution, for example) is refluxed with excess alcohol. The resulting two-phase azeotrope with water
- 35 separates at the top of a fractionating column into a lower aqueous phase, which is removed, and the alcohol which returns to the column as reflux. This quickly

provides a solution of the desired potassium alkoxide. A hydrocarbon or ether having a higher boiling point than the alcohol used is added, and the excess alcohol is distilled off. What remains is an alcohol-free  
5 potassium alkoxide, partly suspended in the hydrocarbon, partly dissolved.

The reaction of acetylenic hydrocarbons with carbonyl compounds is preferably carried out using alcohol-free  
10 potassium alkoxides. However, the presence of alcohol is generally not a problem.

The base used is a mixture of KOH and potassium alkoxide or pure potassium alkoxide. For example, the  
15 weight ratio of KOH to potassium butoxide is preferably within the range from 30 : 70 to 0 : 100% by weight, particularly preferably within the range from 5 : 95 to 1 : 99% by weight. Very particular preference is given to a KOH-to-potassium butoxide ratio of 1 : 99% by  
20 weight.

The reaction temperature is generally within the range from 0 to 50°C, preferably within the range from 20 to 30°C. It is particularly preferable to conduct the  
25 reaction at about 30°C.

In a preferred embodiment, the first step is to prepare a suspension of potassium base and solvent. This is followed by the ketone and acetylene, or the ketone and  
30 the alkynemonool, being synchronously introduced in the appropriate molar ratio into the suspension of potassium base and solvent. The resulting reaction mixtures are efficiently stirrable in customary stirred tanks. The reaction time depends inter alia on the  
35 amount of starting materials used. It is for example within the range from 4 to 8 hours, preferably 6 hours, when 1 mol of base is used. The ketone and the

acetylene or the alkynemonool are preferably added synchronously in the course of 4 hours and subsequently stirred together for 2 hours. After the reaction has ended, the batch is hydrolyzed with water, and most of the base passes into the aqueous phase as KOH. The resulting KOH solution can be removed by phase separation. The useful materials remain in the organic phase and, after hydrolysis and subsequent neutralization (preferably with glacial acetic acid), can be isolated by distillation. The solvent which is removed in the course of the distillation can be reused.

In the process of the invention, the reaction mixture is efficiently stirrable during the entire reaction. High yields of generally not less than 70%, preferably not less than 80%, are obtained as a result.

The Examples which follow illustrate the invention.

#### Examples

##### Inventive Example 1 - Preparation of dimethylhexynediol:

A jacketed reactor equipped with a stirrer is charged with 114 g of xylene and 112 g of potassium isobutoxide (1 mol) [c(base)=5mol/l]. The suspension is heated to 30°C and maintained at that temperature during the reaction. 58 g of acetone (1 mol) and 13 g of acetylene (0.5 mol) are passed in concurrently over 4 hours. Following a post-reaction period of 2 h, the batch is hydrolyzed with 120 g of water. Following removal of the organic phase and neutralization with 7 g of glacial acetic acid, 61.5 g of dimethylhexynediol (corresponding to an 86% yield) are isolated from a

conversion of 98% (based on acetone). In addition, the alkynemonool methylbutynol is obtained in a 4% yield.

#### Comparative Example 1

5

A jacketed reactor equipped with a stirrer is charged with 376 g of xylene and 97 g of potassium isobutoxide (0.87 mol) [ $c(\text{base})=1.8\text{mol/l}$ ]. The suspension is heated to 30°C and maintained at that temperature during the  
10 reaction. 92 g of acetone (1.59 mol) and 20 g of acetylene (0.77 mol) are passed in concurrently over 4 hours. Following a post-reaction period of 2 h, the batch is hydrolyzed with 105 g of water. Following removal of the organic phase and neutralization with  
15 0.7 g of glacial acetic acid, 58.7 g of dimethylhexynediol (corresponding to a 52% yield) are isolated from a conversion of 86% (based on acetone). In addition, the alkynemonool methylbutynol is obtained in a 14.4% yield.

20

#### Comparative Example 2 (EP-A 0 285 755)

A jacketed reactor equipped with a stirrer is charged with 350 g of methyl tert-butyl ether and 74 g of  
25 potassium hydroxide powder (85%). The suspension is heated to 20°C and maintained at that temperature during the reaction. 69.9 g of acetone and 15.6 g of acetylene are passed in concurrently over 4 hours. Following a post-reaction period of 1 h, the batch is  
30 hydrolyzed with 150 g of water. Following removal of the organic phase and neutralization with 13 g of glacial acetic acid, 61.3 g of dimethylhexynediol (corresponding to a 72% yield) are isolated from a conversion of 92% (based on acetone). The reaction  
35 batch became unstirrably solid toward the end of the reaction.

**Inventive Example 2 - Preparation of dimethylhexynediol  
via methylbutynol**

5 A jacketed reactor equipped with a stirrer is charged  
with 114 g of xylene and 112 g of potassium isobutoxide  
(1 mol). The suspension is heated to 30°C and  
maintained at that temperature during the reaction.  
29 g of acetone (0.5 mol) and 42 g of methylbutynol  
(0.5 mol) are passed in concurrently over 4 hours.  
10 Following a post-reaction period of 2 h, the batch is  
hydrolyzed with 120 g of water. Following removal of  
the organic phase and neutralization with 13 g of  
glacial acetic acid, 58.7 g of dimethylhexynediol  
(corresponding to an 83% yield) are isolated from a  
15 conversion of 98% (based on acetone).

**Comparative Example 3**

20 A jacketed reactor equipped with a stirrer is charged  
with 114 g of xylene and 112 g of potassium isobutoxide  
(1 mol). The suspension is heated to 30°C and  
maintained at that temperature during the reaction.  
55.1 g of acetone (0.95 mol) and 80 g of methylbutynol  
(0.95 mol) are passed in concurrently over 4 hours.  
25 Following a post-reaction period of 2 h, the batch is  
hydrolyzed with 120 g of water. Following removal of  
the organic phase and neutralization with 21 g of  
glacial acetic acid, 93 g of dimethylhexynediol  
(corresponding to a 69% yield) are isolated from a  
30 conversion of 93% (based on acetone). In addition, the  
alkynemonool methylbutynol is obtained in a 14.3%  
yield.



**Inventive Example 3 - Preparation of 4,7-dihydroxy-2,4,7,9-tetramethylhex-5-yne:**

A jacketed reactor equipped with a stirrer is charged  
5 with 310 g of xylene and 224 g of potassium isobutoxide  
(2 mol). The suspension is heated to 30°C and  
maintained at that temperature during the reaction.  
200 g of methyl isobutyl ketone (2 mol) and 26 g of  
10 acetylene (1 mol) are passed in concurrently over  
4 hours. Following a post-reaction period of 2 h, the  
batch is hydrolyzed with 230 g of water. Following  
removal of the organic phase and neutralization with  
glacial acetic acid, 330 g of 4,7-dihydroxy-2,4,7,9-  
15 tetramethylhex-5-yne (corresponding to a 73% yield) are  
isolated from a conversion of 89% (based on acetone).

Concentration dependence of selectivity of reaction of  
acetone with acetylene to form dimethylhexynediol using  
a suspension of potassium isobutoxide in xylene at  
20 various weight ratios between the potassium base in  
xylene and acetone

**Inventive Example 4 - Preparation of dimethylhexynediol  
(potassium base in xylene/acetone = 6.4)**

25 A jacketed reactor equipped with a stirrer is charged  
with 228 g of xylene and 112 g of potassium  
isobutoxide. The suspension is heated to 30°C and  
maintained at that temperature during the reaction.  
30 53.3 g of acetone and 11.7 g of acetylene are passed in  
concurrently over 4 hours. Following a post-reaction  
period of 2 h, the batch is hydrolyzed with 120 g of  
water. Following removal of the organic phase and  
neutralization with 13 g of glacial acetic acid, 57.1 g  
35 of dimethylhexynediol (corresponding to an 88% yield)  
are isolated from a conversion of 98%. In addition, the  
alkynemonool methylbutynol is obtained in a 7% yield.

**Inventive Example 5 - Preparation of dimethylhexynediol  
(potassium base in xylene/acetone = 4.5):**

5 A jacketed reactor equipped with a stirrer is charged  
with 114 g of xylene and 112 g of potassium  
isobutoxide. The suspension is heated to 30°C and  
maintained at that temperature during the reaction.  
53.3 g of acetone and 11.7 g of acetylene are passed in  
10 concurrently over 4 hours. Following a post-reaction  
period of 2 h, the batch is hydrolyzed with 120 g of  
water. Following removal of the organic phase and  
neutralization with 11 g of glacial acetic acid, 56.7 g  
of dimethylhexynediol (corresponding to an 87% yield)  
15 are isolated from a conversion of 98%. In addition, the  
alkynemonool methylbutynol is obtained in a 7% yield.

**Inventive Example 6 - Preparation of dimethylhexynediol  
(potassium base in xylene/acetone = 3.6):**

20 A jacketed reactor equipped with a stirrer is charged  
with 80 g of xylene and 112 g of potassium isobutoxide.  
The suspension is heated to 30°C and maintained at that  
temperature during the reaction. 53.5 g of acetone and  
25 11.7 g of acetylene are passed in concurrently over  
4 hours. Following a post-reaction period of 2 h, the  
batch is hydrolyzed with 120 g of water. Following  
removal of the organic phase and neutralization with  
15 g of glacial acetic acid, 51.8 g of  
30 dimethylhexynediol (corresponding to a 79% yield) are  
isolated from a conversion of 98%. In addition, the  
alkynemonool methylbutynol is obtained in a 5% yield.

**Inventive Example 7 - Preparation of dimethylhexynediol  
(potassium base in xylene/acetone = 3.2)**

A jacketed reactor equipped with a stirrer is charged  
5 with 114 g of xylene and 224 g of potassium  
isobutoxide. The suspension is heated to 30°C and  
maintained at that temperature during the reaction.  
107 g of acetone and 23.4 g of acetylene are passed in  
concurrently over 4 hours. Following a post-reaction  
10 period of 2 h, the batch is hydrolyzed with 240 g of  
water. Following removal of the organic phase and  
neutralization with 18 g of glacial acetic acid, 91.6 g  
of dimethylhexynediol (corresponding to a 70% yield)  
are isolated from a conversion of 98%. In addition, the  
15 alkynemonool methylbutynol is obtained in a 4% yield.

5 *As enclosed to IPER*

ART 34/ADD1

We claim:-

1. In a process for preparing alkynediols by reacting ketones with acetylenic hydrocarbons selected from the group consisting of acetylene and alkynemonool in an organic solvent in the presence of a base comprising potassium alkoxides of primary and/or secondary alcohols to form adducts of alkynemonools and/or alkynediols and said base which precipitate from the reaction mixture, the improvement which comprises, using as acetylenic hydrocarbon acetylene in the ratio of ketone to acetylene from 1,9 to 2,1 : 1 and the ratio of potassium alkoxide to ketone is within the range from 0,9 to 2,1 : 1 and using as acetylenic hydrocarbon alkynemonool in the ratio of alkynemonool to ketone from 1 : 0,8 to 1,2 and the ratio of potassium alkoxide to ketone is within the range from 1,5 to 2,2 : 1, so as to produce gellike adducts having a spherical surface, whereby the reaction mixture remains stirrable during the entire reaction.
2. A process as claimed in claim 1, wherein, using as acetylenic hydrocarbon acetylene, it is used in a stoichiometric amount with regard to the ketone and the ratio of potassium alkoxide to ketone is within the range from 1 : 1 to 1,5 : 1.
3. A process as claimed in claim 2, wherein the ratio of potassium alkoxide to ketone is within the range from 1.1 : 1 to 1.3 : 1.
4. A process as claimed in claim 1, wherein, using as acetylenic hydrocarbon alkynemonool the ratio of alkynemonool to ketone is within the range from 1 : 1 and the ratio of potassium alkoxide to ketone is within the range from 1,9 : 1 to 2,1 : 1.
5. A process as claimed in any of claims 1 to 4, wherein ketones selected from acetone, methyl isobutyl ketone and cyclohexanone are used.
6. A process as claimed in claim 5, wherein acetone is used as ketone.

- 5 7. A process as claimed in any of claims 1 to 6, wherein hydrocarbons are used as solvents.
8. A process as claimed in any of claims 1 to 7, wherein the potassium alkoxides used are potassium butoxides.

# Declaration, Power of Attorney

Page 1 of 3

0050/049288

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Preparation of alkynediols

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_

☒ was filed as PCT international application

Number PCT/EP99/05933 ✓

on 13/08/1999 ✓

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.

Country

Day/Month/Year

Priority  
Claimed

19837211.6 ✓

Germany ✓

17 August 1998 ✓

☒ Yes ☐ No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(c) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

**Application Serial No.**

**Filing Date**

**Status (pending, patented,  
abandoned)**

|       |       |       |
|-------|-------|-------|
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |
| _____ | _____ | _____ |

2 And we (I) hereby appoint **Messrs. HERBERT. B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1-00 Alois Kindler  
NAME OF INVENTOR

Alois Kindler  
Signature of Inventor

Date 6/11/2000

Goethestr. 81  
67165 Waldsee  
Germany DEX  
Citizen of: Germany ✓  
Post Office Address: same as residence

2-00 Melanie Brunner  
NAME OF INVENTOR

Melanie Brunner  
Signature of Inventor

Date 6/11/2000

Anton-Bruckner-Str.10  
67105 Schifferstadt  
Germany DEX  
Citizen of: Germany ✓  
Post Office Address: same as residence

3-00 Christian Tragut  
NAME OF INVENTOR

Christian Tragut  
Signature of Inventor

Date 6/11/2000

Erlenweg 19  
67157 Wachenheim  
Germany DEX  
Citizen of: Germany ✓  
Post Office Address: same as residence

4-00 Jochem Henkelmann  
NAME OF INVENTOR

Jochem Henkelmann  
Signature of Inventor

Date 6/11/2000

Bassermannstr.25  
68165 Mannheim  
Germany DEX  
Citizen of: Germany ✓  
Post Office Address: same as residence